

Fundamental-measure density functional for the fluid of aligned hard hexagons: New insights in fundamental measure theory

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In this article we obtain a fundamental measure functional for the model of aligned hard hexagons in the plane. Our aim is not just to provide a functional for a new, admittedly academic, model, but to investigate the structure of fundamental measure theory. A model of aligned hard hexagons has similarities with the hard disk model. Both share “lost cases”, i.e. admit configurations of three particles in which there is pairwise overlap but not triple overlap. These configurations are known to be problematic for fundamental measure functionals, which are not able to capture their contribution correctly. This failure lies in the inability of these functionals to yield a correct low density limit of the third order direct correlation function. Here we derive the functional by projecting aligned hard cubes on the plane $x + y + z = 0$. The correct dimensional crossover behavior of these functionals permits us to follow this strategy. The functional of aligned hard cubes, however, does not have lost cases, so neither had the resulting functional for aligned hard hexagons. The latter exhibits, in fact, a peculiar structure as compared to the one for hard disks. It depends on a uniparametric family of weighted densities through a new term not appearing in the functional for hard disks. Apart from studying the freezing of this system, we discuss the implications of the functional structure for new developments of fundamental measure theory.

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I. INTRODUCTION

Fundamental measure (FM) theory [1] is one of the most successful density functional (DF) theories, yet also one of the most difficult to adapt to new systems. Unlike classical DF approximations [2], which describe a general approximate recipe in which some knowledge of the fluid is “cooked up” to produce a functional, FM theory constructs functionals from geometric principles in a far more involved manner. As a result of this process the resulting functionals have got nicer features; among them, three are striking: their higher predictive power (they yield structure functions that are needed as input in classical approximations), their natural formulation for multicomponent mixtures, and their good behavior under dimensional crossover (when d -dimensional systems are constrained to $d - 1$ dimensions, d -dimensional FM functionals become $(d - 1)$ -dimensional ones). However, the price to pay for having such nice functionals is that their structure is extremely rigid: almost any reasonable modification one makes to “improve” the quality of the results spoils one of the above features, mainly dimensional crossover [3, 4, 5]. The latter is not only a remarkable property that FM functionals (and only them) share with exact ones, but also a desirable property of any functional which is meant to study fluids under strong confinement [6, 7, 8].

This is the reason why every extension of FM theory beyond the hard spheres fluid for which it was origi-

nally proposed [1, 9, 10] has become a “major achievement”. Extensions are nowadays available for parallel hard cubes and parallelepipeds [11, 12, 13, 14] (which provide a restricted orientation model of liquid crystals [15]); soft spherical potentials [16]; non-additive mixtures [17, 18, 19]; mixtures of rods, plates and spheres [20, 21, 22, 23, 24]; lattice fluids [25, 26, 27, 28, 29, 30, 31]; and fluids in porous media [32, 33, 34]. Even for hard spheres, Rosenfeld’s original functional [1] has undergone important improvements over the years [35, 36, 37, 38], after realizing that dimensional crossover was a unique feature of this type of functionals very much entangled to its construction procedure.

When Rosenfeld first conceived FM theory [1] it rested strongly on geometrical properties of spherical overlaps and on scaled-particle theory [39]. A decade later, the theory had been reformulated in terms of “zero-dimensional (0D) cavities” [35, 36]. By this it must be understood a cavity able to hold no more than a hard sphere. Under the requirement that confinement of the FM functional to one such cavity must lead to the exact result, and introducing one- two- and three-point cavities, by adding and subtracting the necessary terms so as to maintain the exact 0D limit a functional arises with the required structure [37, 38]. The result is not “perfect” in the sense that there are three-point 0D cavities for which the exact result cannot be recovered: those for which three spheres placed at the three points of the cavity have pairwise overlap but not triple overlap. These cavities were termed “lost cases” [37] because they do not contribute to the free energy, and their existence reveals the inability of this construction to reproduce the lowest order in the density expansion of the three-particle direct correlation function (DCF) [5] (which is non-zero for those configurations). As

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a matter of fact, the problems arising from the extension of this functional to mixtures of hard spheres have the same origin, and corrections trying to palliate these problems are unable to remedy the defect of the correlations [5].

On the contrary, the FM functional for aligned hard parallelepipeds does not have lost cases because for this kind of particles, whenever three particles have pairwise overlap there is necessarily triple overlap. In fact, the exact 0D limit is recovered for cavities of any shape [12], and the low-density limit of the three-particle DCF is exact. This led to the belief that FM theory is simply unable to produce a functional for hard spheres without lost cases [5].

The extension of FM theory to lattice fluids is based on this 0D cavity reformulation [25, 26, 27, 28, 29, 30, 31]. But because lattice geometry lacks spherical symmetry, this extension has uncovered an important ingredient in the theory. While the FM functional for hard spheres is expressed in terms of a set of weighted densities whose weights are associated to geometrical features of the *particles* [1, 9, 10, 35, 36, 37, 38], the weights in lattice FM functionals are associated to geometrical features of *maximal 0D cavities* [26, 29, 30]. These are 0D cavities such that if they get extended in any way, they are not 0D cavities anymore [41]. Maximal 0D cavities need not have the same shape as the particles that define them (in most cases they will not); for instance, maximal 0D cavities of a nearest-neighbor exclusion lattice gas in a triangular lattice, which is represented by hard hexagons, are equilateral triangles (see Ref. [28] for this and other examples). At the same time, by construction these lattice FM functionals recover the exact 0D limit for *any* 0D cavity [29, 30] and as a consequence of this fact, they can be proven to yield the correct low-density limit of the three-particle DCF [30]. Interestingly, maximal 0D cavities for aligned hard parallelepipeds have exactly the same shape as the particles, however this is not true for spheres, where apart from spherical cavities there are other maximal 0D cavities with different shapes (see Fig. 1 for an example).

In Ref. [28] FM functionals for many two- and three-dimensional hard core lattice gases were obtained from the known functional of hard (hyper)cubes in a (hyper)cubic lattice by exploiting dimensional crossover. One of these was the hard hexagons model, which was obtained from the hard cubes model by constraining the centers of mass of the cubes to lay on the plane $x + y + z = 0$. In this paper we will apply the same procedure to the continuum FM functional of parallel hard cubes in order to obtain the (continuum) two-dimensional fluid of aligned hard hexagons. The reason to do this is the following. Three aligned hard hexagons can be arranged in such a way that there is pairwise overlap but no triple overlap (see Fig. 2); hence, according to the cavity construction of the FM functional for hard spheres [37, 38], there should be “lost cases”. However, we are going to obtain such

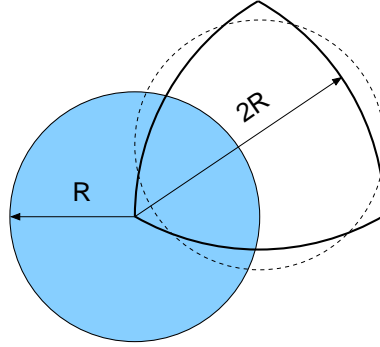


FIG. 1: (color online) Example of a non-spherical maximal 0D cavity for the system of two-dimensional hard spheres (disks) of radius R (colored circle in the figure). Any rotation of this cavity will produce a new maximal 0D cavity. To illustrate that this cavity is not contained in a spherical maximal 0D cavity, the latter is plotted on top with dashed line.

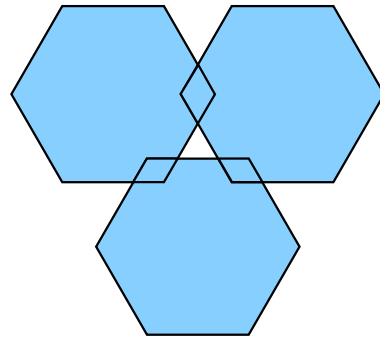


FIG. 2: (color online) Configuration of three aligned hexagons exhibiting pairwise, but not triple overlap (lost cases).

a functional by dimensional crossover from the functional of parallel hard cubes which *does not* have lost cases. As explained, this means that the 0D limit is recovered for any 0D cavity; therefore the same will hold for the resulting functional for aligned hard hexagons.

The FM functional for aligned hard hexagons that we will obtain provides interesting insights into FM theory. First of all, the maximal 0D cavities, not the particles, are the relevant constructive geometrical object. Secondly, it points out that a FM functional for hard spheres (or disks) will probably have an infinite number of terms. From a practical point of view this is good and bad news: good, because we know what the FM functional for hard spheres [38] is missing in order to get rid of the lost cases; bad because a functional with an infinite number of terms will be useless for real purposes. At the end of this paper we will discuss these issues in more depth. We think, however, that despite its eventual utility, the information that this FM functional for aligned hard hexagons provides is relevant for a thorough understanding of FM theory.

The rest of the paper is organized as follows. In section II we describe the construction of the FM

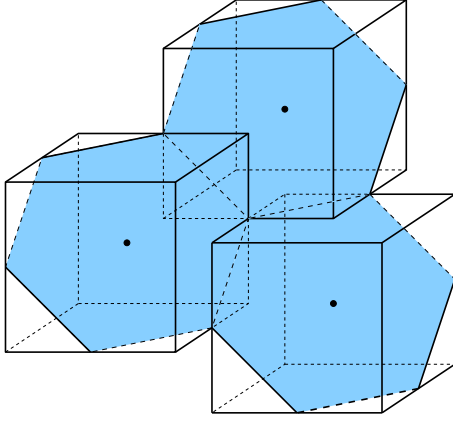


FIG. 3: (color online) Constraining the centers of mass of parallel hard cubes to lay on the plane $x + y + z = 0$ yields a system of aligned hard hexagons.

functional for aligned hard hexagons by dimensional crossover of the FM functional for the fluid of parallel hard cubes. The procedure as well as the resulting weighted densities and the form of the functional are explained in this section, but the detailed calculations are deferred to Appendix A. In Sec. III we analyze the equation of state derived from the functional both for the uniform fluid and for the triangular solid phase. The functional predicts a first order freezing at coexisting packing fractions $\eta_f = 0.58$ for the fluid and $\eta_s = 0.63$ for the solid. Finally, in section IV we discuss the features of the resulting functional, with special emphasis on those that cause the functional to be free from lost cases.

II. FROM HARD CUBES TO HARD HEXAGONS

As described in Ref. [28] the way to obtain an effective system of aligned hard hexagons is to start off from a system of hard cubes aligned parallel to the coordinate axes and constraint their centers of mass to lay on the plane $x + y + z = 0$. Figure 3 illustrates this geometrical construction. Making use of the good behavior of FM functionals under any dimensional crossover, we will carry out the same projection in the FM functional of parallel hard cubes and thus obtain the one for aligned hexagons.

The FM functional of parallel hard cubes of edge-length $2L$ can be written as [12, 13]

$$F_{\text{PHC}}[\tilde{\rho}] = F_{\text{PHC}}^{\text{id}}[\tilde{\rho}] + F_{\text{PHC}}^{\text{ex}}[\tilde{\rho}], \quad (1)$$

where

$$\beta F_{\text{PHC}}^{\text{id}}[\tilde{\rho}] = \int d\mathbf{r} \tilde{\rho}(\mathbf{r}) (\ln \mathcal{V} \tilde{\rho}(\mathbf{r}) - 1) \quad (2)$$

is the ideal contribution (\mathcal{V} is the thermal volume and $\beta = (kT)^{-1}$, with k the Boltzmann constant and T the

temperature) for a density profile of the hard cube fluid $\tilde{\rho}(\mathbf{r})$, and

$$\beta F_{\text{PHC}}^{\text{ex}}[\tilde{\rho}] = \int d\mathbf{r} \Phi_{\text{PHC}}(\{p_\alpha(\mathbf{r})\}), \quad (3)$$

with

$$\Phi_{\text{PHC}} = \Phi_{\text{PHC}}^{(1)} + \Phi_{\text{PHC}}^{(2)} + \Phi_{\text{PHC}}^{(3)}, \quad (4)$$

$$\Phi_{\text{PHC}}^{(1)} = -\frac{1}{8} p_0 \ln(1 - p_3), \quad (5)$$

$$\Phi_{\text{PHC}}^{(2)} = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{8(1 - p_3)}, \quad (6)$$

$$\Phi_{\text{PHC}}^{(3)} = \frac{p_{2,1} p_{2,2} p_{2,3}}{8(1 - p_3)^2}, \quad (7)$$

is the excess, over the ideal, free energy. The functions $p_\alpha(\mathbf{r})$ are weighted densities

$$p_\alpha(\mathbf{r}) = \int d\mathbf{r}' \omega_\alpha(\mathbf{r} - \mathbf{r}') \tilde{\rho}(\mathbf{r}'), \quad (8)$$

where the scalar or vectorial weights are given by

$$\omega_3(\mathbf{r}) = \tau(x)\tau(y)\tau(z), \quad (9)$$

$$\omega_2(\mathbf{r}) = (\zeta(x)\tau(y)\tau(z), \tau(x)\zeta(y)\tau(z), \tau(x)\tau(y)\zeta(z)), \quad (10)$$

$$\omega_1(\mathbf{r}) = (\tau(x)\zeta(y)\zeta(z), \zeta(x)\tau(y)\zeta(z), \zeta(x)\zeta(y)\tau(z)), \quad (11)$$

$$\omega_0(\mathbf{r}) = \zeta(x)\zeta(y)\zeta(z), \quad (12)$$

with

$$\tau(u) = \Theta(L - |u|), \quad \zeta(u) = \delta(L - |u|), \quad (13)$$

$\Theta(x)$ being Heaviside's step function (0 if $x < 0$ and 1 if $x > 0$) and $\delta(x)$ Dirac's delta. Notice that $p_{2,j}$ ($j = 1, 2, 3$) denotes the j th component of \mathbf{p}_2 .

Now, the projection amounts to taking

$$\tilde{\rho}(\mathbf{r}) = \rho(\mathbf{x}) \delta(x + y + z) \quad (14)$$

in the functional (1), where $\rho(\mathbf{x}) = \rho(x, y)$ is the density profile of aligned hard hexagons. The choice of coordinates corresponds to a change to the (non-orthogonal) basis $\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\}$ given by $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3) = (\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3) P$, with

$$P = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & -1 & 1 \end{pmatrix} \quad (15)$$

and $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$ the canonical basis. Vectors \mathbf{b}_1 and \mathbf{b}_2 form a basis on the plane $x + y + z = 0$ (see Fig. 4). This choice of vectors amounts to working with the projections of the hexagons on the XY plane, because the projections of \mathbf{b}_1 and \mathbf{b}_2 are simply \mathbf{e}_1 and \mathbf{e}_2 .

The details of introducing the density profile (14) into the excess part of the free-energy functional are deferred to Appendix A. Here we simply give the final

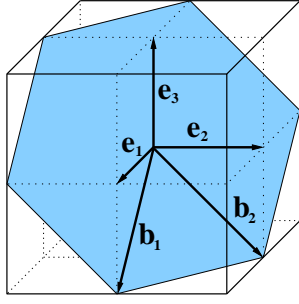


FIG. 4: (color online) Choice of an appropriate basis on the plane $x + y + z = 0$ to represent the coordinates of the hexagons.

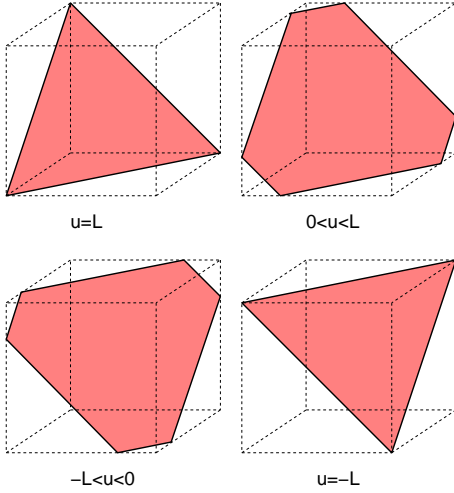


FIG. 5: (color online) Maximal 0D cavities for the system of aligned hard hexagons are obtained as the sections of the cubes by planes $x + y + z + u = 0$ with $-L \leq u \leq L$. Triangular cavities correspond to $u = \pm L$ while hexagonal ones to $-L < u < L$ ($u = 0$ is the regular hexagon).

result. The projection transforms the original weighted densities for the cubes, $p_\alpha(\mathbf{r})$, into a set of new densities for the hexagons. The most striking result is that these new weighted density are associated to maximal 0D cavities for the hexagons, not to the hexagons themselves. The complete set of such maximal 0D cavities can be obtained as the sections of one of the original cubes by the planes $x + y + z + u = 0$, where $-L \leq u \leq L$ (see Fig. 5). The cases $u = \pm L$ correspond to two equilateral triangles (pointing up and down), while the cases $-L < u < L$ correspond to hexagons (of which only $u = 0$ is a regular hexagon identical to the fluid particles). This comes as an important difference with respect to the FM functional for hard spheres, and in retrospect yields a new interpretation to the weighted densities of the original cubes as associated to maximal 0D cavities (which in the case of cubes are indistinguishable from the particles).

To be precise, the weighted densities that we need to

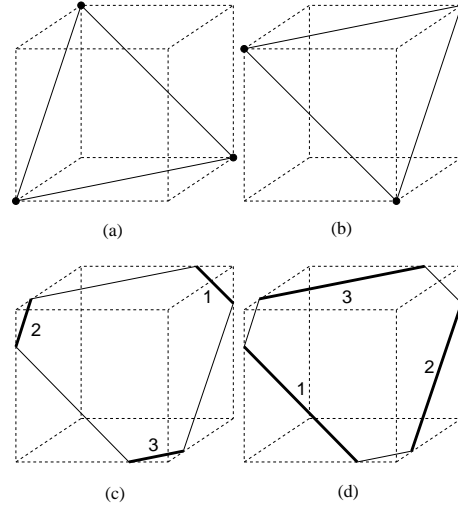


FIG. 6: Weighted densities are associated to geometric elements of the cavities: $n_0^{(+)}(\mathbf{x})$ (a) and $n_0^{(-)}(\mathbf{x})$ (b) to the vertices of the triangular cavities; the components of $\mathbf{n}_1^{(+)}(\mathbf{x}, u)$ (c) and $\mathbf{n}_1^{(-)}(\mathbf{x}, u)$ (d) to the edges of the cavities. In (c) and (d) the numbers 1, 2, 3 label the component which is associated to each edge.

express the functional are

$$n_0^{(\pm)}(\mathbf{x}) = \int d\mathbf{x}' \Omega_0^{(\pm)}(\mathbf{x} - \mathbf{x}') \rho(\mathbf{x}'), \quad (16)$$

$$\mathbf{n}_1^{(\pm)}(\mathbf{x}, u) = \int d\mathbf{x}' \Omega_1^{(\pm)}(\mathbf{x} - \mathbf{x}', u) \rho(\mathbf{x}'), \quad (17)$$

$$n_2(\mathbf{x}, u) = \int d\mathbf{x}' \Omega_2(\mathbf{x} - \mathbf{x}', u) \rho(\mathbf{x}'), \quad (18)$$

and it is convenient to define also the weighted densities

$$\mathbf{n}_1^{(\pm)}(\mathbf{x}) = \mathbf{n}_1^{(\pm)}(\mathbf{x}, \pm L), \quad (19)$$

$$n_2^{(\pm)}(\mathbf{x}) = n_2(\mathbf{x}, \pm L). \quad (20)$$

The weights that define these densities are the following:

$$\begin{aligned} \Omega_0^{(\pm)}(\mathbf{x}) = & \delta(x \mp L) \delta(y \mp L) \\ & + \delta(x \mp L) \delta(y \pm L) \\ & + \delta(x \pm L) \delta(y \mp L), \end{aligned} \quad (21)$$

$$\begin{aligned} \Omega_1^{(\pm)}(\mathbf{x}, u) = & \left(\delta(x \mp L) \tau(y) \tau(u - x - y), \right. \\ & \tau(x) \delta(y \mp L) \tau(u - x - y), \\ & \left. \tau(x) \tau(y) \delta(u - x - y \mp L) \right), \end{aligned} \quad (22)$$

$$\Omega_2(\mathbf{x}, u) = \tau(x) \tau(y) \tau(u - x - y). \quad (23)$$

The meaning of these weighted densities is related to averages over different geometric elements of the maximal 0D cavities to which they are associated. Thus, $n_2(\mathbf{x}, u)$ is the average over the area of the cavity corresponding to that value of u (the colored regions in

Fig. 5); each component of $\mathbf{n}_1^{(\pm)}(\mathbf{x}, u)$ is the average over one edge of the hexagonal cavity (triangular if $u = \pm L$); and $n_0^{(\pm)}(\mathbf{x})$ is the average over the three vertices of the corresponding triangular cavity. The two latter cases are illustrated in Fig. 6.

With the help of these weighted densities we can write $\beta F_{\text{AHH}}^{\text{ex}}[\rho] = \int d\mathbf{x} \Phi_{\text{AHH}}(\mathbf{x})$, where

$$\Phi_{\text{AHH}} = \Phi_{\text{AHH}}^{(1)} + \Phi_{\text{AHH}}^{(2)} + \Phi_{\text{AHH}}^{(3)}, \quad (24)$$

$$\Phi_{\text{AHH}}^{(1)} = -\frac{1}{6} \sum_{\pm} n_0^{(\pm)} \ln(1 - n_2^{(\pm)}), \quad (25)$$

$$\Phi_{\text{AHH}}^{(2)} = \frac{1}{6} \sum_{\pm} \frac{n_{1,1}^{(\pm)} n_{1,2}^{(\pm)} + n_{1,2}^{(\pm)} n_{1,3}^{(\pm)} + n_{1,3}^{(\pm)} n_{1,1}^{(\pm)}}{1 - n_2^{(\pm)}}, \quad (26)$$

$$\Phi_{\text{AHH}}^{(3)} = \frac{1}{2} \sum_{\pm} \int_{-L}^L du \frac{n_{1,1}^{(\pm)}(u) n_{1,2}^{(\pm)}(u) n_{1,3}^{(\pm)}(u)}{[1 - n_2(u)]^2}. \quad (27)$$

(For the sake of notational simplicity we have omitted the argument \mathbf{x} in all weighted densities, retaining only the argument u in those that depend on it.)

There are several features worth noticing in this FM functional for aligned hard hexagons which we have derived from the one for parallel hard cubes. First of all, the most obvious fact: weighted densities are associated to the geometry of maximal 0D cavities, as in lattice FM functionals, and not to the geometry of particles, as in the FM functional for hard spheres or disks. Secondly, as in the system of aligned hard hexagons there is an infinity of maximal 0D cavities, the third term exhibits a “sum” over them all; hence the integral in that term. Finally, the typical FM structure for Φ as a sum of D terms, D being the dimension of the problem, breaks down here: we have a *two*-dimensional system which is described as a sum of *three* terms.

All these features will have consequences for the general structure of FM functionals, which we shall discuss later in Sec. IV

III. THERMODYNAMICS OF THE FLUID OF ALIGNED HARD HEXAGONS

A. Fluid phase

The free energy of the fluid phase is obtained by specializing the weighted densities with a uniform particle density. The only subtle point we have to take into account is that, because of our choice of coordinates (which actually describe the projections of hexagons on the XY plane) if ρ denotes the particle density of hexagons (measured on the plane $x + y + z = 0$), the uniform density profile will reduce to $\rho(\mathbf{x}) = \sqrt{3}\rho$. (This $\sqrt{3}$ is the scale factor difference between actual hexagons and their projections.) With this in mind, and

given that the area of a hexagon is $v_h = 3\sqrt{3}L^2$ (recall that L is half the edge length of the cubes), hence the packing fraction $\eta = v_h\rho$, the weighted densities reduce in this limit to

$$n_0 = \eta/L^2, \quad (28)$$

$$\mathbf{n}_1^{(\pm)}(u) = \frac{\eta}{3L} \left(1 \pm \frac{u}{L}\right) (1, 1, 1), \quad (29)$$

$$\mathbf{n}_1^{(\pm)} = \frac{2\eta}{3L} (1, 1, 1), \quad (30)$$

$$n_2(u) = \left(1 - \frac{u^2}{3L^2}\right) \eta, \quad (31)$$

$$n_2^{(\pm)} = \frac{2\eta}{3}, \quad (32)$$

where the packing fraction $\eta = v_h\rho$, and therefore the excess free energy per unit volume (in kT units), Φ , becomes

$$\begin{aligned} \frac{\Phi}{\rho} = & -\ln\left(1 - \frac{2\eta}{3}\right) + \frac{\eta}{3(1-\eta)} + \left(3 - \frac{8}{3}\eta\right) \\ & \times \sqrt{\frac{\eta}{3(1-\eta)^3}} \tan^{-1} \sqrt{\frac{\eta}{3(1-\eta)}}. \end{aligned} \quad (33)$$

From this expression we can obtain the equation of state as

$$\begin{aligned} \frac{\beta p}{\rho} = & 1 + \eta \frac{\partial(\Phi/\rho)}{\partial \eta} \\ = & \frac{1 - \eta/2}{(1 - \eta)^2} + \left(\frac{3}{2} - \eta\right) \\ & \times \sqrt{\frac{\eta}{3(1-\eta)^5}} \tan^{-1} \sqrt{\frac{\eta}{3(1-\eta)}}. \end{aligned} \quad (34)$$

Perhaps the most striking feature of this equation of state is its divergence as $(1 - \eta)^{-5/2}$ at close packing. This exponent 2.5 is noticeably higher than the exponent 2 that a straightforward scaled particle argument would predict.

B. Solid phase

The standard way to approach the solid phase in DF theory is to use a parametrization of the density profile as a sum of Gaussians centered at the nodes of the solid lattice,

$$\hat{\rho}(\mathbf{x}') = \frac{\theta\alpha}{\pi} \sum_{r_1, r_2 \in \mathbb{Z}} \exp\left\{-\alpha(\mathbf{x}' - r d\mathbf{a}_1 - s d\mathbf{a}_2)^2\right\}. \quad (35)$$

Here $\hat{\rho}(\mathbf{x}')$ denotes the density profile of hexagons on the plane $x + y + z = 0$; $\mathbf{x}' = (x', y')$ denotes the position referred to an orthogonal coordinate system on that plane; α is related to the mean square displacement of the particle with respect to its lattice node; θ is the occupancy of the solid (the mean number of particles in one unit cell), which accounts for the vacancies;

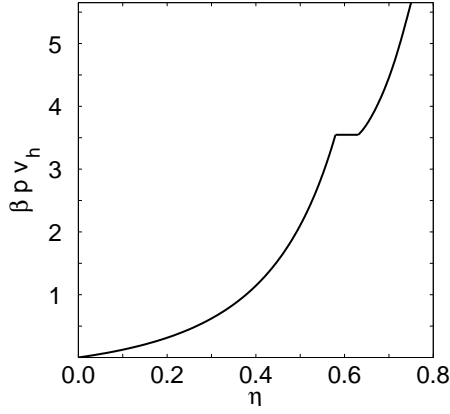


FIG. 7: Reduced pressure, $\beta p v_h$, with $v_h = 3\sqrt{3}L^2$ the area of a hexagon, versus packing fraction $\eta = \rho v_h$ for a fluid of aligned hard hexagons. The packing fractions at coexistence are $\eta_f = 0.58$ for the fluid and $\eta_s = 0.63$ for the solid.

and $d = d_c \sqrt{\theta/\eta}$ is the lattice parameter, with η the packing fraction and d_c the lattice parameter at close packing, $d_c = \sqrt{6}L$ (hexagons have edge length $\sqrt{2}L$). The unit vectors $\mathbf{a}'_1 = (0, 1)$ and $\mathbf{a}'_2 = (-\sqrt{3}/2, 1/2)$ are a convenient choice for the basis of the triangular lattice's unit cell.

Although the implementation of this density profile is rather straightforward, a few words on the appropriate choice of variables may be helpful. First of all, as all weighted densities are expressed in terms of projected coordinates on the plane XY, we should describe the density profile in terms of these coordinates. Thus we can write $\mathbf{x}' = J\mathbf{x}$, with

$$J = \begin{pmatrix} \sqrt{2} & \sqrt{1/2} \\ 0 & \sqrt{3/2} \end{pmatrix}, \quad (36)$$

and, given that $\det J = \sqrt{3}$, the density profile becomes $\rho(\mathbf{x}) = \sqrt{3}\hat{\rho}(\mathbf{x}')$. In the projected representation, the unit cell is a rhombus, so it is convenient to introduce in the integrals the change of variables $\mathbf{x} \rightarrow Q\mathbf{x}$, where

$$Q = \frac{1}{\sqrt{6}} \begin{pmatrix} -1 & -2 \\ 2 & 1 \end{pmatrix}. \quad (37)$$

This transforms the global integral as

$$\int_{\text{unit cell}} d\mathbf{x} \longrightarrow \frac{1}{2} \int_{-d/2}^{d/2} dx \int_{-d/2}^{d/2} dy \quad (38)$$

(notice that $\det Q = 1/2$).

In the projected coordinates, the sum of Gaussians defining the density profile can be factorized as

$$\rho(\mathbf{x}) = \sqrt{3}\theta \sum_{r_1, r_2 \in \mathbb{Z}} g_\alpha\left(\frac{x_{r_1}}{2} + y_{r_2}\right) g_\alpha\left(\frac{\sqrt{3}x_{r_1}}{2}\right), \quad (39)$$

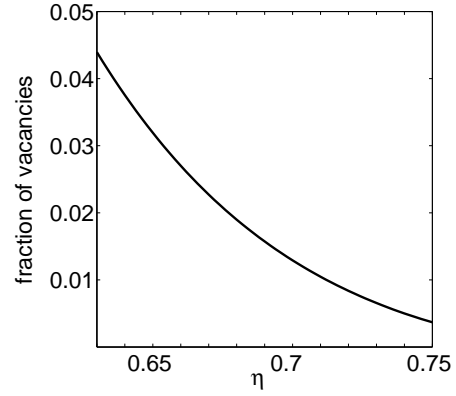


FIG. 8: Fraction of vacancies, $1 - \theta$, as a function of the packing fraction η for the fluid phase.

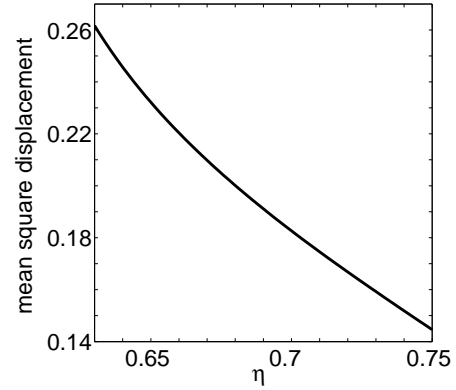


FIG. 9: Mean square displacement of particles around the equilibrium positions in the solid phase, as a function of the packing fraction η .

with the definitions $x_{r_1} = x - r_1 d$, $y_{r_2} = y - r_2 d$ and $g_\alpha(x) = \sqrt{\alpha/\pi} e^{-\alpha x^2}$. This permits one to express the weighted densities as products of Gaussian and error functions.

Minimization of the functional is carried out numerically in the parameters α and θ . This determines the free energy of the solid phase for every packing fraction η . At the point where this free-energy curve branches off the one of the fluid phase, the slope discontinuously decreases. This produces a concavity in the whole free-energy curve and therefore the transition is first order and the coexisting densities are determined via a standard Maxwell's double-tangent construction. The resulting equation of state, depicting both the fluid and the solid pressures, is plotted in Fig. 7. Also plotted in Figs. 8 and 9 are the fraction of vacancies, $1 - \theta$, and the square root of the mean square displacement of hexagons with respect to their lattice positions. Interestingly, the solid of hard hexagons has a low fraction of vacancies all the way up from the transition (never larger than 5%), in marked contrast with what happens for the fluid of hard cubes from which the functional for this system is derived [14].

One last remark is in order. The result found here for the equation of state of the system of aligned hard hexagons is very similar to that of its lattice counterpart [28]. For the latter the exact result is known to have a continuous transition [40], although so smooth that a first order discontinuity is not a bad quantitative approximation. The exact result for the continuum model is unknown, but certainly the same caveat on the nature of the transition applies to it.

IV. DISCUSSION

The fluid of aligned hard hexagons has strong similarities with the fluid of hard disks. The most important for the aims of this work is that particles may be placed in configurations such that they have pairwise overlap but not triple overlap (see Fig. 2). These configurations have been termed “lost cases” [37] because FM theory, as currently formulated for hard spheres or hard disks [37, 38], is unable to capture their contribution. The basic constructive principle of FM theory is the recovery of the exact 0D limit of the free energy when the system is constraint to any 0D cavity. Lost cases arise in certain 0D cavities (for instance, for hard disks, a circular cavity of radius larger than R and smaller than $2R/\sqrt{3}$) and thus the FM functional does not recover the exact limit for them. This failure of the theory is associated to an incorrect low density limit of the third order direct correlation function [5]; in other words, the density expansion of the FM functional for hard disks or spheres is incorrect already at third order.

The logic of the construction of FM functional for d -dimensional hard spheres requires that the excess free energy density be a sum of d terms [37]

$$\Phi_{d\text{-HS}} = \Phi_{d\text{-HS}}^{(1)} + \Phi_{d\text{-HS}}^{(2)} + \cdots + \Phi_{d\text{-HS}}^{(d)}. \quad (40)$$

Further terms constructed on the same logic are identically zero. Each of these terms is incorporated starting from the first one and trying to compensate for the spurious terms that arise when two, three, etc., particles are incorporated to a 0D cavity. When there are lost cases, the last one vanishes and thus cannot bring about its compensation. The logic of this construction strongly relies on the fact that weights have the same shape of the particles, as in Rosenfeld’s original FM theory [1], of which this new constructive method is just a generalization.

Applying the same logic to the fluid of aligned hard hexagons would lead to the same result and lost cases would arise. Yet, there is another method to obtain the FM functional for such a fluid, which is the projection we have carried out in this work of the fluid of parallel hard cubes on a specific plane. The latter fluid does not have lost cases because of the particular form of its particles (if there is pairwise overlap between three cubes, there is necessarily triple overlap as well), and this nice property is inherited by the functional for the hexagons.

As a matter of fact, the resulting functional has a different structure in several respects. First of all, there is a weighted density for every one of the maximal 0D cavities conceivable for this system. These include two triangles and a continuum of irregular hexagons. Because of this, weighted densities depend on a parameter that gauges the shape of the cavity. This feature is not new: it was revealed in the study of FM functionals for lattice models [26, 27, 28, 29, 30]. But second and more importantly, there appears a new term, say a “ $d+1$ term”, thanks to which the compensation to recover the exact 0D limit for any 0D cavity is guaranteed. As explained above, this term cannot be predicted by applying the construction logic of the hard disk functional.

Actually both features are connected: there is an extra term because there are several 0D maximal cavities that contribute weighted densities to the functional. What this is telling us is that the functional for hard disks or hard spheres is simply incomplete. Cavities such as that shown in Fig. 1 (and possibly other) should make their contribution through new weighted densities. Notice in passing that any rotation of the cavity of the figure is a new, different, 0D cavity and so there should also be a continuum of weighted densities, as for the hexagons. And accordingly, new terms beyond $\Phi_{d\text{-HS}}$ are to be expected. How many of them? We do not have a definitive answer to this question, but we will provide convincing arguments that there will be infinitely many.

The projection we have carried out from three-dimensional cubes to aligned hard hexagons can be generalized to obtain a FM functional for $2l$ -gons in a straightforward manner. For instance, projections of the fourth-dimensional system of hard hypercubes on the appropriate plane generates octagons. In general, projecting l -dimensional hypercubes on an appropriate plane generates aligned hard $2l$ -gons. Because of the structure of the fluid of parallel hard hypercubes [12] we know that such functionals will have l terms. Disks are obtained as the limit $l \rightarrow \infty$ of $2l$ -gons, so in this limit, the FM functional will be an infinite series. It might happen that the series can be summed up and produce just a single (more complex) term, but this can hardly be foreseen.

So, should we seek for a FM functional for hard disks or hard spheres without lost cases? Well, from the arguments above we believe that it would be a pointless task, for even if we could overcome the difficulty of its construction, we would probably end up with an extremely cumbersome functional, useless for practical purposes. This does not mean that perhaps including some, not all, the missing terms we could obtain improvements on the current functional. This point might be worth exploring in the future.

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APPENDIX A: PROJECTION OF THE FM FUNCTIONAL FOR PARALLEL HARD CUBES ON THE PLANE $x + y + z = 0$

1. Dimensional crossover

Using the projection on the XY plane defined by $\mathbf{r} \rightarrow P\mathbf{r}$, with P given by (15),

$$\beta F_{\text{PHC}}^{\text{ex}}[\tilde{\rho}] = \int d\mathbf{r} \Phi_{\text{PHC}}(\{p_\alpha(P\mathbf{r})\}), \quad (\text{A1})$$

where

$$p_\alpha(P\mathbf{r}) = \int d\mathbf{r}' \omega_\alpha(P(\mathbf{r} - \mathbf{r}')) \tilde{\rho}(P\mathbf{r}'), \quad (\text{A2})$$

with the weights defined in (9)–(12). According to (14), in the projected coordinates

$$\tilde{\rho}(P\mathbf{r}) = \rho(\mathbf{x})\delta(z). \quad (\text{A3})$$

This transformation in the density profile allows us to integrate in z' , so the weighted densities become

$$p_\alpha(P\mathbf{r}) = \int d\mathbf{x}' \omega_\alpha(P(\mathbf{x} - \mathbf{x}'), z) \rho(\mathbf{x}'), \quad (\text{A4})$$

where we are expressing a three-component vector as $\mathbf{r} = (\mathbf{x}, z)$. From the previous equation one can define a new set of weighted densities $\{n_\alpha\}$, which depend on a parameter u that corresponds to the z coordinate of the above expression,

$$n_\alpha(\mathbf{x}, u) \equiv \int d\mathbf{x}' \Omega_\alpha(\mathbf{x} - \mathbf{x}', u) \rho(\mathbf{x}'), \quad (\text{A5})$$

with $\alpha = 0, 1, 2$ and Ω_α a scalar or vector function given by

$$\Omega_2(\mathbf{x}, u) = \omega_3(P(\mathbf{x}, u)), \quad (\text{A6})$$

$$\Omega_1(\mathbf{x}, u) = \omega_2(P(\mathbf{x}, u)), \quad (\text{A7})$$

$$\Omega_0(\mathbf{x}, u) = \omega_1(P(\mathbf{x}, u)), \quad (\text{A8})$$

$$\Omega_0(\mathbf{x}, u) = \omega_0(P(\mathbf{x}, u)). \quad (\text{A9})$$

The next step is to obtain the resulting excess free energy after the projection. In order to do that, unnecessary degrees of freedom must be eliminated, which in this particular case amounts to integrating the z coordinate in the PHC functional. Consider the first term (5). Here the integration is immediate, because Ω_0 is sum of Dirac's deltas [42]. Thus we obtain

$$\Phi_{\text{AHH}}^{(1)} = -\frac{1}{8} \sum_{\pm} n_0^{(\pm)} \ln(1 - n_2^{(\pm)}), \quad (\text{A10})$$

with $n_0^{(\pm)}$ and $n_2^{(\pm)}$ defined by (16) and (18), respectively.

For the second and third terms in (3), direct substitution of n_α leads to

$$\Phi_{\text{AHH}}^{(2)} = \frac{1}{8} \int du \frac{\mathbf{n}_0(u) \cdot \mathbf{n}_1(u)}{1 - n_2(u)}, \quad (\text{A11})$$

$$\Phi_{\text{AHH}}^{(3)} = \frac{1}{8} \int du \frac{n_{1,1}(u)n_{1,2}(u)n_{1,3}(u)}{[1 - n_2(u)]^2} \quad (\text{A12})$$

Here $n_\alpha(u)$ is a shorthand for $n_\alpha(\mathbf{x}, u)$. Notice that the integration limits in the above formulas are determined by the support of the weighted density n_2 , which is a product of Heaviside's step functions. It is easy to check that this support is $|u| \leq 3L$. Hence, according to the expression for $n_2(u)$, maximal 0D cavities are recovered (see Fig. 5) when $|u| \leq L$, but when $L \leq |u| \leq 3L$ the corresponding cavities are not maximal. The appearance of these non-maximal 0D cavities is a result of our projection procedure, but the functional cannot explicitly depend on them because any information they provided is, by definition, already accounted for by the maximal 0D cavities. In what follows we will explain how to get rid of these spurious contributions.

2. Elimination of spurious terms

We will show here how to eliminate non-maximal 0D cavities through integration by parts. To this purpose we introduce the following notation: the weight Ω_1 can be decomposed as follows (in what follows we will omit the dependence on (\mathbf{x}, u) for simplicity, introducing only a dependence on u whenever ambiguity might arise)

$$\Omega_1 = \Omega_1^{(+)} + \Omega_1^{(-)}, \quad (\text{A13})$$

where $\Omega_1^{(\pm)}$ has the same expression as Ω_1 in terms of functions τ y ζ , but replacing $\zeta(x)$ with $\delta(x \mp L)$, respectively. New weighted densities $\mathbf{n}_1^{(\pm)}$ can also be introduced associated to these weights. These densities have the properties that $\mathbf{n}_1^{(+)}$ vanishes when $-3L \leq u \leq -L$, whereas $\mathbf{n}_1^{(-)}$ does it when $L \leq u \leq 3L$.

Let us introduce now the differential operator

$$\mathbf{D} \equiv \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial u}, \frac{\partial}{\partial y} + \frac{\partial}{\partial u}, \frac{\partial}{\partial u} \right). \quad (\text{A14})$$

Acting on n_2 results in

$$\mathbf{D}n_2 = -\mathbf{n}_1^{(+)} + \mathbf{n}_1^{(-)}. \quad (\text{A15})$$

As of now, we will only consider the term $\Phi_{\text{AHH}}^{(3)}$ for $-3L \leq u \leq -L$, which will be denoted $\Phi_{\text{AHH}}^{(3,1)}$. According to (A15), in this interval the integrand of $\Phi_{\text{AHH}}^{(3,1)}$ can be written as

$$\begin{aligned} \Phi_0'''(n_2)n_{1,1}^{(-)}n_{1,2}^{(-)}n_{1,3}^{(-)} = \\ \frac{1}{3} \sum_{\sigma \in \Pi_3^+} (D_{\sigma(1)}\Phi_0''(n_2)) n_{1,\sigma(2)}^{(-)}n_{1,\sigma(3)}^{(-)}, \end{aligned} \quad (\text{A16})$$

where Π_3^+ is the set of all the permutations σ of $\{1, 2, 3\}$ with positive signature. Using this identity we can integrate by parts to obtain

$$\begin{aligned} \Phi_{\text{AHH}}^{(3,1)} = \frac{n_{1,1}^{(-)}n_{1,2}^{(-)} + n_{1,2}^{(-)}n_{1,3}^{(-)} + n_{1,3}^{(-)}n_{1,1}^{(-)}}{24[1 - n_2^{(-)}]} \\ - \frac{1}{24} \int_{-3L}^{-L} du \Phi_0''(n_2) \sum_{\sigma \in \Pi_3^+} D_{\sigma(1)} \left(n_{1,\sigma(2)}^{(-)}n_{1,\sigma(3)}^{(-)} \right) (u). \end{aligned} \quad (\text{A17})$$

Notice that in the first term, the components of $\mathbf{n}_1^{(-)}$ without explicit dependence on u refer to those of $\mathbf{n}_1^{(-)}(\mathbf{x}, -L)$, as in (19). The second term in the expression above can be simplified taking into account the new identity

$$D_{\sigma(2)}n_{1,\sigma(3)}^{(-)} + D_{\sigma(3)}n_{1,\sigma(2)}^{(-)} = 2n_{0,\sigma(1)}. \quad (\text{A18})$$

Recall that \mathbf{n}_0 is defined through the weight (A8). Besides,

$$\begin{aligned} \sum_{\sigma \in \Pi_3^+} D_{\sigma(1)} \left(n_{1,\sigma(2)}^{(\pm)}n_{1,\sigma(3)}^{(\pm)} \right) = \\ \sum_{\sigma \in \Pi_3^+} n_{1,\sigma(1)}^{(\pm)} \left(D_{\sigma(2)}n_{1,\sigma(3)}^{(\pm)} + D_{\sigma(3)}n_{1,\sigma(2)}^{(\pm)} \right), \end{aligned} \quad (\text{A19})$$

so substitution of (A18) and (A19) into (A17) allows us to get

$$\begin{aligned} \Phi_{\text{AHH}}^{(3,1)} = \frac{n_{1,1}^{(-)}n_{1,2}^{(-)} + n_{1,2}^{(-)}n_{1,3}^{(-)} + n_{1,3}^{(-)}n_{1,1}^{(-)}}{24[1 - n_2^{(-)}]} \\ - \frac{1}{12} \int_{-3L}^{-L} du \Phi_0''(n_2) \mathbf{n}_0(u) \cdot \mathbf{n}_1^{(-)}(u). \end{aligned} \quad (\text{A20})$$

Moreover, as $\mathbf{D} \cdot \mathbf{n}_0 = 0$ and $\Phi_0''(n_2)\mathbf{n}_1^{(-)} = \mathbf{D}\Phi_0'(n_2)$, a new integration by parts in the integral above yields

$$\begin{aligned} \Phi_{\text{AHH}}^{(3,1)} = \frac{n_{1,1}^{(-)}n_{1,2}^{(-)} + n_{1,2}^{(-)}n_{1,3}^{(-)} + n_{1,3}^{(-)}n_{1,1}^{(-)}}{24[1 - n_2^{(-)}]} \\ + \frac{1}{12} n_0^{(-)} \ln(1 - n_2^{(-)}). \end{aligned} \quad (\text{A21})$$

By symmetry, an identical formula can be obtained when $L \leq u \leq 3L$, but with the weighted densities $n_\alpha^{(+)}$ instead of $n_\alpha^{(-)}$. Doing exactly the same partial integration in (A11) for any $L \leq |u| \leq 3L$ and gathering all the contributions, we arrive at the result

$$\begin{aligned} \Phi_{\text{AHH}} = \Phi_{\text{AHH}}^{\text{res}} - \frac{1}{6} \sum_{\pm} n_0^{(\pm)} \ln(1 - n_2^{(\pm)}) + \\ \frac{1}{24} \sum_{\pm} \frac{n_{1,1}^{(\pm)}n_{1,2}^{(\pm)} + n_{1,2}^{(\pm)}n_{1,3}^{(\pm)} + n_{1,3}^{(\pm)}n_{1,1}^{(\pm)}}{1 - n_2^{(\pm)}}, \end{aligned} \quad (\text{A22})$$

where the residual contribution $\Phi_{\text{AHH}}^{\text{res}}$ is given by

$$\begin{aligned} \Phi_{\text{AHH}}^{\text{res}} = \frac{1}{8} \int_{-L}^L du \frac{\mathbf{n}_0(u) \cdot \mathbf{n}_1(u)}{1 - n_2(u)} + \\ \frac{1}{8} \int_{-L}^L du \frac{n_{1,1}(u)n_{1,2}(u)n_{1,3}(u)}{[1 - n_2(u)]^2}. \end{aligned} \quad (\text{A23})$$

Because of the range $-L \leq u \leq L$ of these integrals, Eq. (A22) only contains contributions from maximal 0D cavities, as required.

A third integration by parts in the residual term will allow us to write the functional in a more compact way. According to (A15), whenever $|u| \leq L$ we can write

$$\mathbf{n}_1 = 2\mathbf{n}_1^{(\pm)} \pm \mathbf{D}n_2. \quad (\text{A24})$$

Then the last integral in (A23) can be expressed in a symmetric form combining $\mathbf{n}_1^{(\pm)}$,

$$\frac{1}{16} \int_{-L}^L du \Phi_0'''(n_2) \sum_{\pm} \prod_{j=1}^3 \left(2n_{1,j}^{(\pm)} \pm D_j n_2 \right) (u). \quad (\text{A25})$$

We now expand the product above and realize three things. First, that the product containing three derivatives vanishes. Second, that cross terms containing one or two derivatives can be integrated with the aid of (A15) and

$$D_{\sigma(2)}n_{1,\sigma(3)}^{(\pm)} + D_{\sigma(3)}n_{1,\sigma(2)}^{(\pm)} = \pm n_{0,\sigma(1)}, \quad (\text{A26})$$

which holds for all $|u| \leq L$. These terms cancel the first one of (A23) and generate a boundary term identical to the last one in (A22). This operation justifies the numerical coefficient appearing in (26). Third, the remaining term, which contains products of the three components of $\mathbf{n}_1^{(\pm)}$, produces (27). This way we arrive at the final form of the functional (24)–(27).

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